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UNITED STATES DEPARTMENT OF THE INTERIOR

BUREAU OF MINES
HELIUM ACTIVITY
DIVISION OF RESEARCH

INTERNAL REPORT

Factors Affecting Hydrogen Adsorptive Capacities of Activated Charcoal and Synthetic Silicates

BY

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BRANCH Process and Equipment Development

PROJECT NO. 1540

DATE May 2, 1957

AMARILLO, TEXAS

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INTRODUCTION

Activated charcoal maintained at -300° F. is used for the final purification of helium. Helium, entering the charcoal columns at 2700 p.s.i.g., contains approximately 0.71 percent nitrogen and 0.03 percent hydrogen as contaminants at the Amarillo plant (see Table I). The charcoal column adsorbs these contaminants and helium leaving the column has a purity of better than 99.99 percent. When the adsorbing column has reached its capacity for hydrogen as indicated by a USBM hydrogen recorder on the output from the column, it is taken offstream for reactivation. A study of the factors affecting the hydrogen adsorptive capacities of the charcoal columns was undertaken in an effort to improve the purification process by reducing the column reactivation times, increasing the adsorptive capacities of the columns, or improving the column efficiencies by the use of synthetic silicates as supplementary adsorbent materials

OBJECTIVE

The objectives of the present investigation were to determine the optimum operating procedures for the most efficient utilization of the activated charcoal columns under plant conditions and to explore the possibility of using synthetic silicates as adsorbents to remove contaminants from helium.

SUMMARY AND CONCLUSIONS

Various samples of helium admixed with other gases were prepared to test the adsorptive capacities of charcoal and several synthetic

silicates or molecular sieves. Molecular sieves, as designated by the manufacturer, are crystaline zeolites: Type 4A is a sodium alumino silicate; and Type 5A is a calcium alumino silicate. The composition of 13X is unknown. The hydrogen adsorptive capacities of these silicates determined at liquid air temperature and various pressures were plotted to show the relative efficiency of each. In high-pressure, nitrogen-hydrogen contaminated helium, 5A is the best hydrogen adsorbing sieve. Test results (See Graph No. 1) for the various pressures indicated that charcoal is far superior to any of the molecular sieves as a hydrogen adsorber. Consequently, to replace or supplement the charcoal with silicate sieves would not be as satisfactory as the use of charcoal filled vessels.

It was determined that the usefulness of charcoal as an adsorbent could be increased if reactivation of contaminated charcoal were to be accomplished at temperatures in excess of 300° F. An equally effective and more practical production procedure is to warm the vessel to room temperature and purge with Grade-A helium. The charcoal purifier should also be prepressured with Grade-A helium before going onstream.

The most striking experimental data indicate that the adsorptive capacity of activated charcoal for hydrogen is materially reduced when interferring nitrogen is in excess of 0.1 percent. Graph III represents the sharp reduction in hydrogen adsorptive capacity when the nitrogen contaminant is increased from 0.02 percent to 0.96 percent. Graph III

indicates that maximum hydrogen adsorption by charcoal would occur when no interferring nitrogen was present. However, complete removal of nitrogen from our 99.5% Helium would require a drastic and unwarranted alteration of our production process.

Although the charcoal purifiers are monitored for hydrogen saturation, their basic function is nitrogen adsorption. During the same time that a charcoal purifier becomes saturated with hydrogen, it also adsorbs a far greater amount of nitrogen. A determination of the actual adsorptive capacity of charcoal for nitrogen from a helium-nitrogen gas would establish whether or not it is more ecconomical to remove all hydrogen prior to the charcoal vessels, and monitor the "Grade-A" stream for nitrogen, than to continue the present system.

GENERAL CONSIDERATIONS

I. The use of charcoal in plant operations:

Nearly all the information available in the literature concerning the adsorptive capacity of charcoals is for low partial pressures of pure gases and has been determined under static conditions. No information is available on the adsorptive capacity of charcoal for one particular gas from a flowing high-pressure gas mixture. One of the objectives of this investigation was to determine the adsorptive capacity of charcoal for hydrogen from flowing high-pressure helium-hydrogen-nitrogen mixtures.

Activated charcoal, maintained at -300° F. is used for the final purification of helium. The helium, entering the charcoal columns at 2700 p.s.i.g., contains approximately 0.71 percent nitrogen and 0.03 percent hydrogen as contaminants (See Table I). The charcoal in the columns adsorbs these contaminants and the helium leaving the column has a purity of better than 99.99 percent. When one column has reached its capacity for hydrogen as indicated by a USBM hydrogen recorder on the output, it is taken off the stream for reactivation. At the Amarillo plant, charcoal is reactivated by the following method: the vessel is taken off the stream and periodically depressured to 200 p.s.i.g. as the vessel warms; desorption of contaminants from the charcoal is speeded by warming the vessel with nitrogen to a temperature of about 50° F.; after doing this the vessel is purged with 99.5 percent helium and the vessel is pressured up to 2700 p.s.i.g. with 99.5 percent helium. It is then cooled to -300° F. and returned to service.

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Additional capacity of the charcoal for nitrogen remains after the hydrogen adsorptive capacity has been reached. When the prototype of our present process was set up, modern means of detecting traces of nitrogen were not available. Therefore, in order to determine when the charcoal had reached saturation, it was necessary to monitor the outlet stream for the first traces of hydrogen. Subsequently, when Deoxo units were installed at a later date, a trace of hydrogen was deliberately left in the unpurified helium to continue the hydrogen monitoring system. The impurities average 0.0275 percent hydrogen and 0.71 percent nitrogen. However, these quantities may change for hydrogen from 0.0 to 0.1 or higher and may run as high as 0.95 percent for nitrogen (See Table I.)

II. Possible supplemental or replacement processes:

In an effort to find supplemental or replacement adsorbents for the helium purification cycle, consideration was given to the relatively new alumino silicates or molecular sieves as designated by the manufacturer. The molecular sieves are crystaline zeolites. Four A is a sodium alumino silicate. Five A is a calcium alumino silicate, and the composition of 13X is unknown. The crystaline silicate contains many small cavities with pores of a uniform size. Only molecules small enough to pass through the pores can be adsorbed on the extensive inner surface of the cavity. Numerical designation of sieves represents the pore size of the cavity in angstroms. When originally formed these cavities contained water of hydration. Upon heating, the water is driven off without destroying the uniformity of the pore or collapsing

the cavity. Inquiry of the manufacturer brought a report from Mr. R. A. Jones, Tonawanda Laboratory, Linde Air Products Company, which is quoted in part below:

"The possibility of substituting molecular sieves for activated carbon to remove hydrogen and nitrogen from helium at low temperatures is a very interesting one. Unfortunately, we do not have any very clear-cut answers because we have no hydrogen adsorption data on our molecular sieves. However, if activated carbon is suitable for this application, there are theoretical reasons why molecular sieves might be superior. A search of the literature reveals that adsorption isotherms have been measured for hydrogen on certain naturally occuring zeolites that are somewhat similar to our products. The quantities of hydrogen adsorbed, and these data are at -183° C., are, of course, quite small just as the adsorptive capacity of activated carbon for hydrogen is quite small."

The hydrogen adsorption capacity of activated charcoal and several types of the molecular sieves were determined under similar conditions for comparison.

EXPERIMENTAL SECTION

Apparatus and Experimental Procedure

A stainless steel cylinder with an internal volume of 10 ml. (Style H5-10 manufactured by Hoke, Incorporated) was pressure tested to 2500 p.s.i. @ -300° F. and fitted with 3/16-inch OD copper tubing

lines such that one of the fittings could be removed to fill the cylinder with an adsorbent sample. A valve manifold permitted introduction of either the test gas or a helium purge, an outside vent for reactivation, or bypass of the cylinder for purging the rest of the apparatus with helium. A Baker and Company Deoxo hydrogen analyzer was inserted downstream of the adsorbent cylinder to indicate the first trace of hydrogen passing from the adsorbent. For uniformity, the Deoxo unit was set at maximum sensitivity and the test readings were taken when the Deoxo unit indicated 27.5 p.p.m. hydrogen on a scale of 5.5 p.p.m. per division. A wet test meter downstream of the Deoxo recorded total flow. All the samples were tested at a flow rate of 0.40 cubic feet per hour as required by the Deoxo unit. A sleeve heater (USBM helium apparatus heater manufactured by Refinery Supply Company) was placed around the adsorbent cylinder and the adsorbent samples were reactivated between tests by heating to 500° F. The sample was purged and prepressured with Grade-A helium.

The first series of tests were to determine the optimum reactivation procedure. The above described procedure was found to be best and was employed throughout subsequent experiments. Other experiments at reactivation showed that equally satisfactory results could be obtained by heating at 200-300° F. and purging for a longer period of 15 to 25 minutes, or the sample could be simply exposed to the atmosphere for an overnight or 16-hour period. Laboratory reactivations of charcoal at room temperature produced a fair result when the

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warmup period was slow and the sample was purged extensively with Grade-A helium. Reactivation without purging produced poor results even with heating at 300 and 500° F. Reactivation studies are listed on Table II.

Tests run on activated charcoal, 4A, 5A, and 13X are reported in Table III and the results are compared on Graph I.

Of the molecular sieves 5A was found to be the best hydrogen adsorber in either helium-hydrogen, or Helium-hydrogen-nitrogen admixed gases, at high pressures. Superiority of charcoal over all molecular sieves as a hydrogen adsorber was clearly established. Information furnished by the Linde Air Products Company had indicated that some of the synthetic silicates would be better than charcoal, but our results showed no indication of this.

Various gas samples were prepared to determine the hydrogen adsorptive capacity of charcoal versus sample pressure. The samples contained small amounts of hydrogen and nitrogen as impurities in a helium gas. The composition of the gas samples and the variation in hydrogen adsorptive capacity of the adsorbent with pressure for that particular sample gas is given in Table III, and is plotted on Graph II. In general, the hydrogen adsorptive capacity of the charcoal increased with increasing sample pressure. It was noted that small increases in the amount of nitrogen present caused a marked decrease in the amount of hydrogen adsorbed.

A series of samples were tested at 1000 p.s.i.g. which contained about the same amount of hydrogen, but with percentages of nitrogen

that ranged from 0.02 to 0.96 percent. The results of these tests are plotted on Graph III as the hydrogen adsorptive capacity of the charcoal versus the amount of interferring nitrogen present. As indicated by the curve, the presence of as little as 0.1 percent nitrogen decreased the hydrogen adsorptive capacity of charcoal by 40 percent.

The findings of this investigation establish that our production process could be improved by purging the charcoal vessel with Grade-A helium and prepressuring the vessel with Grade-A helium to 2700 p.s.i.g. before returning it to service. The hydrogen adsorptive capacity of charcoal would be greatly increased if the nitrogen impurity of 99.5 percent helium were completely removed at some point upstream of the charcoal purifier. (See Graph III) This consideration presents numerous problems and may not be practical.

Charcoal is an efficient high capacity nitrogen adsorber. As previously pointed out, the total nitrogen adsorptive capacity for charcoal is never reached when hydrogen is present. A determination of the actual adsorptive capacity of charcoal for nitrogen from a helium-nitrogen gas would establish whether or not it would be more profitable to remove all hydrogen prior to the charcoal vessel and monitor the Grade-A stream for nitrogen, than to continue the present system. Commercially available nitrogen detectors utilizing high sensitivity thermal conductivity cells could be used as monitors. Since the use of charcoal as a nitrogen adsorber rather than a hydrogen adsorber might greatly benefit the Helium Activity, it is the recommendation of

this report that an investigation be conducted to determine the total nitrogen adsorptive capacity of charcoal from a helium-nitrogen gas. This study should also determine the optimum method of removing hydrogen upstream of the charcoal purifier.

TABLE I

Variations of impurities in "99.5% Helium"

Date	Recorder reading	Analysis (MS No.)	% N_2	% H_2	% Helium
4/2/56	99.10	8573	0.95	0.03	99.10
4/9/56	99.25	8598	0.72	0.03	99.25
4/16/56	99.45	8643	0.80	0.02	99.15
4/17/56	99.40	8645	0.79	0.02	99.18
4/17/56	99.40	8724	0.80	0.00	99.20
6/7/56	99.40	8831	0.61	0.02	99.36
9/11/56	99.50	9296	0.60	0.10	99.40
9/21/56	99.50	9370	0.45	0.00	99.55

TABLE II - REACTIVATION TEST

Wt. sample charcoal 0.0108 pounds

Gas No. MS 8600 = 0.37% H_2 0.02% N_2 99.6% He

No.	React Temp.	Purge cu.ft./hr	React. time min.	Ft. 3 passed	P.s.i.g.	ft.3 STP	Y	Remarks
1	72° F.	2	20	3.187	1000	2.565	.879	
2	72° F.	2	20	3.112	800	2.505	.859	
3	72° F.	2	20	3.105	800	2.499	.857	
4	72° F.	2	30	3.148	1000	2.534	.869	
5	500°F.	2	60	3.958	1680	3.186	1.092	
6	72° F.	2	25	3.737	1725	3.008	.994	
7	300°F.	2	60	4.038	1775	3.250	1.114	
8	300°F.	2	45	3.937	1812.5	3.169	1.086	
9	72° F.	2	16	3.616	1862.5	2.910	.998	
10	72° F.	5	10	3.012	1887.5	2.424	.451	
11	72° F.	-	60	0.175	1900	.140	.026	Depressured once
12	72° F.	-	-	3.662	1925	2.947	.549	Overnight exposure
13	72° F.	-	30	0.165	1900	.132	.024	Depressured several times to 200 p.s.i.g.
14	72° F.	-	-	3.663	1987.5	2.948	.549	Previously air exposed for months

Note: All adsorptive tests were made when the adsorbent had been cooled by liquid air to about -300° F.

TABLE III EXPERIMENTAL DATA

Calculations

V_1 = gas (ft.^{3}) which wet test meter recorded before adsorbent began to pass hydrogen

$$V_2 = \frac{T_2}{T_1}\frac{P_1}{P_2} V_1$$

$$V_2 = \frac{(273)}{(273+22.2)}\frac{(12.8)}{(14.7)} V_1$$

V_2 = ft.^{3} STP gas stripped of nitrogen and hydrogen which passed through wet test meter.

V_t = Total gas (ft.^{3} STP) applied to adsorbent

$$V_t = \frac{V_2}{(\%\ \text{Helium})}$$

Y = Volume hydrogen (ft.^{3} STP) adsorbed by one pound of adsorbent

$$Y = \frac{V_t\ (\%\ \text{Hydrogen})}{(\text{Lbs. adsorbent})} \quad \text{or } Y = \frac{V_2\ (\%\ \text{Hydrogen})}{(\%\ \text{Helium})\ (\text{Lbs. adsorbent})}$$

TABLE III (Continued)

Gas No. MS 8600 = 0.37% H_2 0.02% N_2 99.6% He

Sample: 4A Weight: 0.01571 pounds

P.s.i.g.	V_1	V_2	Y
200	0.176	0.141	0.051
200	0.184	0.148	0.050
300	0.180	0.144	0.049
300	0.169	0.136	0.046
600	0.322	0.259	0.088
600	0.312	0.251	0.086
1000	0.370	0.297	0.101
1000	0.378	0.304	0.104

Gas No. MS 8602 = 0.33% H_2 0.34% N_2 99.33% He

Sample: 4A Weight: 0.01571 pounds

P.s.i.g.	V_1	V_2	Y
200	0.238	0.191	0.041
200	0.244	0.196	0.042
400	0.302	0.243	0.052
400	0.322	0.259	0.056
600	0.539	0.433	0.093
600	0.509	0.409	0.088

TABLE III (Continued)

Gas No.	MS 8602 =	0.34% H_2	0.33% N_2	99.32 He
Sample: Charcoal		Weight: .01164 pounds		
P.s.i.g.	V_1	V_2	Y	
200	1.167	0.939	0.300	
200	1.092	0.879	0.281	
500	1.523	1.226	0.392	
600	1.676	1.349	0.431	
600	1.735	1.396	0.446	
1000	1.761	1.417	0.453	
1000	1.742	1.402	0.480	
1475	2.687	2.163	0.692	

Gas No.	MS 8791 =	0.32% H_2	0.96% N_2	98.68% He
Sample: Charcoal		Weight: 0.01164 pounds		
P.s.i.g.	V_1	V_2	Y	
1000	1.81	1.457	0.405	
1000	1.808	1.455	0.404	

TABLE III (Continued)

Gas No. MS 8600 =	$0.37\%\ H_2$	$0.02\%\ N_2$	99.60% He
Sample: Charcoal	Weight: 0.01084 pounds		
P.s.i.g.	V_1	V_2	Y
200	1.581	1.272	0.436
200	1.562	1.257	0.431
400	2.237	1.808	0.620
400	2.292	1.845	0.633
600	2.693	2.167	0.743
600	2.663	2.143	0.735
800	3.105	2.499	0.857
800	3.112	2.505	0.859
1000	3.187	2.565	0.879
1000	3.148	2.534	0.869
1680	3.958	3.186	1.092
1725	3.737	3.008	1.031
1775	4.038	3.250	1.114
1812	3.937	3.169	1.086
1837	3.616	2.910	0.998
1887	3.012	2.424	0.831
1925	3.662	2.947	1.010
1982	3.663	2.948	1.011

TABLE III (Continued)

Gas No. 8600 = 0.37% H_2 0.02% N_2 99.6% He

Sample: 5A Weight: 0.01437 pounds

P.s.i.g.	V_1	V_2	Y
200	0.110	0.088	0.022
200	0.140	0.112	0.028
200	0.134	0.107	0.027

Gas No. 8602 = 0.34% H_2 0.33% N_2 99.32% He

Sample: 5A Weight: 0.01344 pounds

P.s.i.g.	V_1	V_2	Y
500	1.432	1.152	0.319
500	1.435	1.155	0.319
1000	1.990	1.600	0.443
1000	1.912	1.539	0.426
1500	1.552	1.249	0.345

Gas No. MS 8600 = 9.37% H_2 0.02% N_2 91.6% He

Sample: 13X Weight: 0.01327 pounds

P.s.i.g.	V_1	V_2	Y.
1000	0.659	0.530	0.181
1000	0.658	0.529	0.181

TABLE III (Continued)

Gas No.	MS 8789 =	0.32% H_2	0.09% N_2	99.59% He
Sample:	Charcoal		Weight:	0.01164 pounds
	P.s.i.g.	V_1	V_2	Y
	1000	2.323	1.870	0.519
	1000	2.266	1.824	0.507

Gas No.	MS 9431 =	0.14% H_2	0.1% N_2	99.76% He
Sample:	Charcoal		Weight:	0.01255
	P.s.i.g.	V_1	V_2	Y
	1000	4.75	3.823	0.424
	1000	4.85	3.904	0.433
	1600	4.95	3.984	0.442
	1600	5.11	4.113	0.456
	2200	6.525	5.252	0.582
	2200	6.475	5.212	0.578

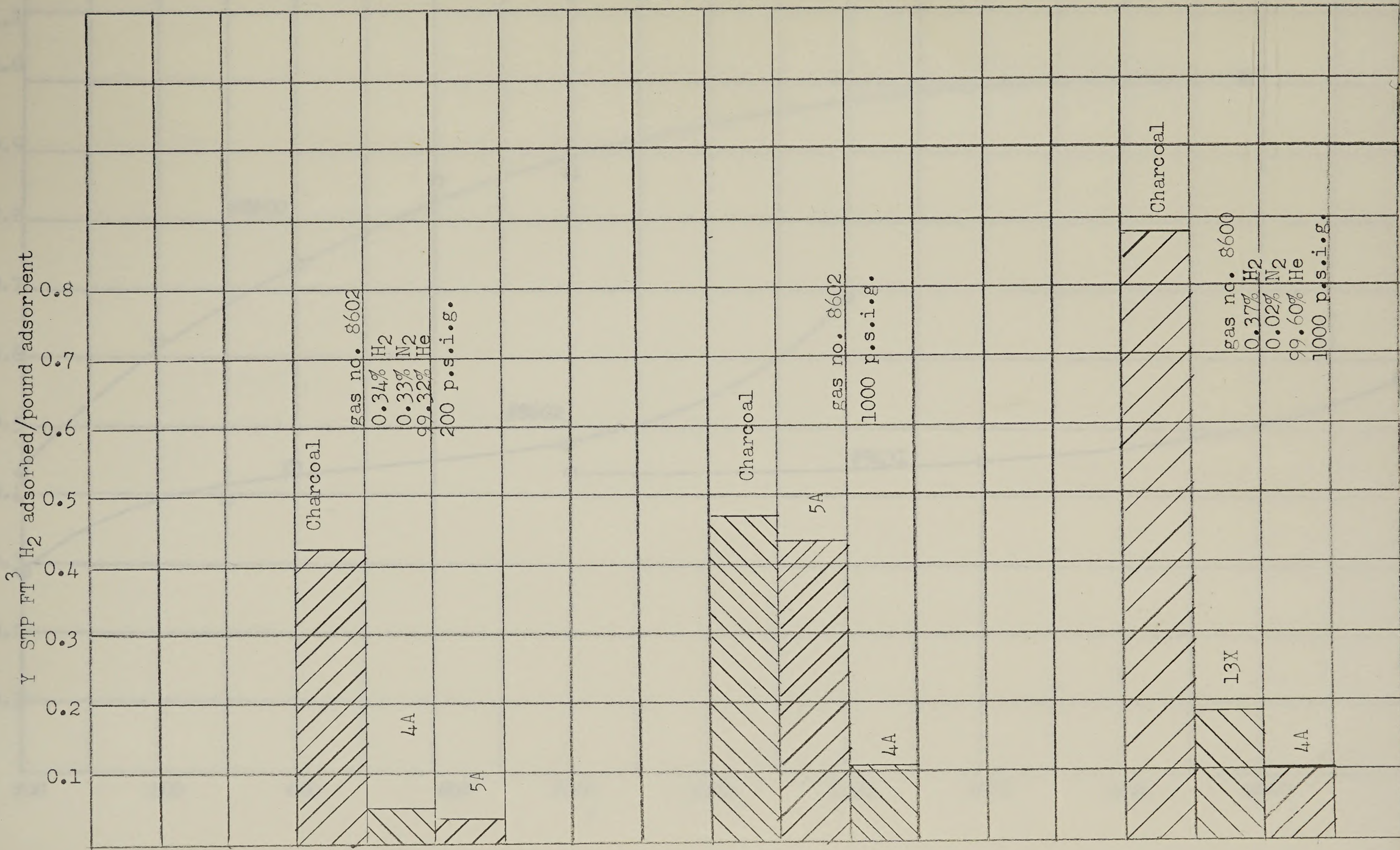
TABLE III (Continued)

Gas No. MS 8602 = 0.33% H_2 0.34% N_2 99.33% He

Sample: 4A Weight: 0.01571 pounds

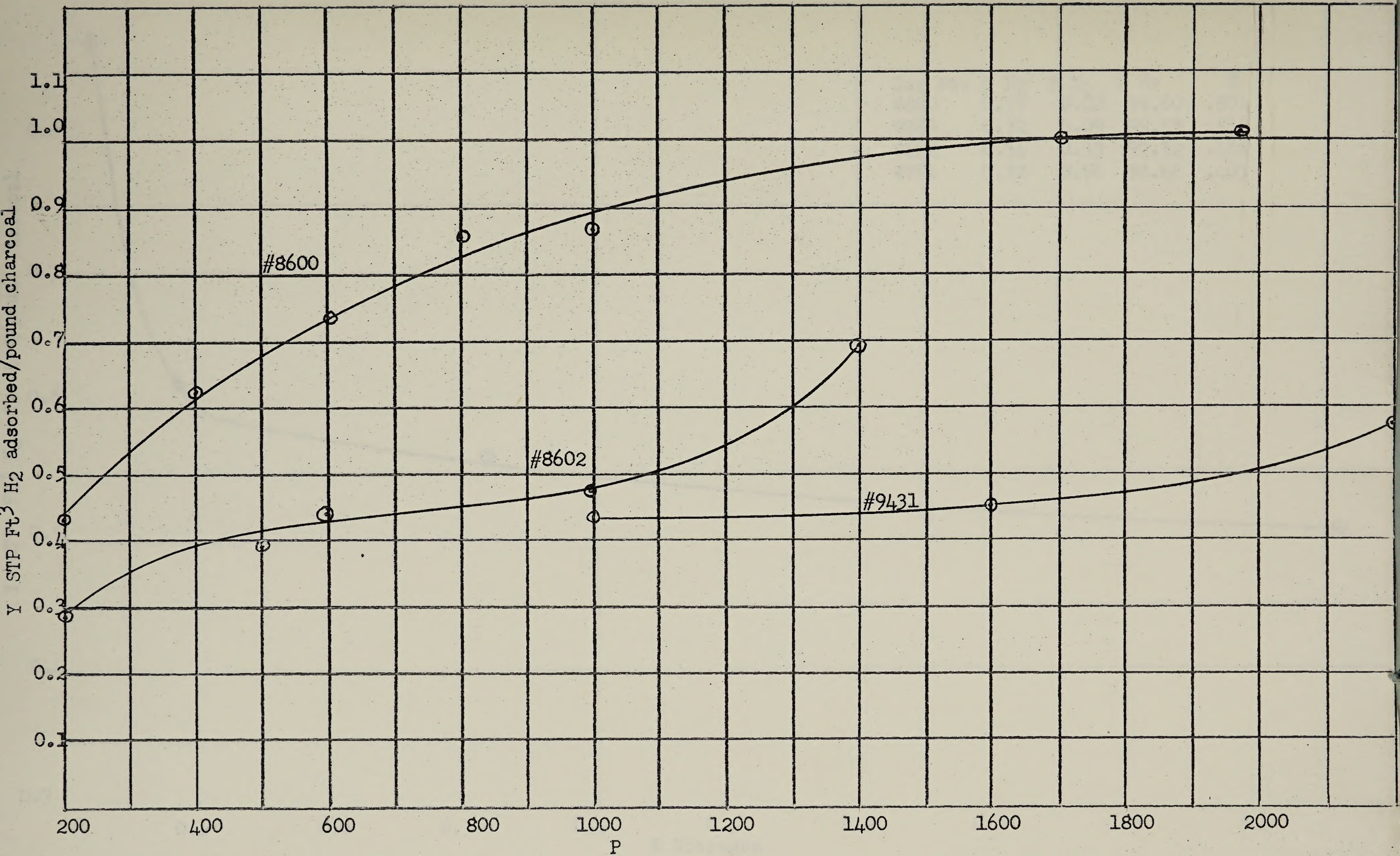
P.s.i.g.	V_1	V_2	Y
1000	0.671	0.540	0.117
1000	0.662	0.532	0.115
1700	0.478	0.384	0.083
1750	0.470	0.378	0.082
1800	0.575	0.462	0.100
2050	0.811	0.652	0.142
2075	0.914	0.735	0.159
2125	0.906	0.729	0.158

GRAPH NO. I



Y STP FT^3 H_2 adsorbed/pound adsorbent
0.8
0.7
0.6
0.5
0.4
0.3
0.2
0.1
Charcoal
4A
5A
gas no. 8602
0.34% H_2
0.33% N_2
99.32% He
200 p.s.i.g.
Charcoal
5A
4A
gas no. 8602
1000 p.s.i.g.
Charcoal
13X
4A
gas no. 8600
0.37% H_2
0.02% N_2
99.60% He
1000 p.s.i.g.

GRAPH II


1.1
1.0
0.9
0.8
0.7
0.6
0.5
0.4
0.3
0.2
0.1
Y STP Ft^3 H_2 adsorbed/pound charcoal
#8600
#8602
#9431
200
400
600
800
1000
1200
1400
1600
1800
2000
P

Charcoal @ 1000 p.s.i.g. Graph III